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COMMENTS FOLLOWING DR. HOUGEN'S PAPER

RELATIONSHIP BETWEEN THE FEASIBLE
GROUP AND THE POINT GROUP OF
A RIGID MOLECULE

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ABSTRACT

The rôle of the point group in conventional rigid molecule theory is reviewed and its relationship to the feasible group discussed.

[†]Work performed under the auspices of the USERDA.

It is very important to understand the relationship between the feasible group of a rigid molecule as discussed in Dr. Hougen's talk and the conventional point group of the molecule. It is my belief that neither of these groups is more fundamental than the other, that both concepts generalize to nonrigid molecules, and that both groups (as well as others) are important in the study of molecular models. This viewpoint will be defended here only for rigid molecules, and in such a way as to complement Dr. Hougen's presentation.

The viewpoint I shall present is the *conventional one* and is developed, for example, in the article by Wilson and Howard (1) and in the book by Wilson, Decius, and Cross (2). I shall, however, emphasize throughout this talk the rôles of the point group and of the moving frame. My colleague, Harold W. Galbraith, and I have developed these details elsewhere (Refs. 3,4), but I believe it to be useful to review again the more essential features of this approach. I shall focus on two aspects of the description of a rigid molecule: (i) the description of the static model (equilibrium configuration) of a molecule; and (ii) the description of the motion of the dynamical model of the molecule in space-time.

Consider first the description of the static model (the dumbbell model made up of rods and spheres). The static model will be described in a laboratory frame L with basis vectors $(\hat{l}_1, \hat{l}_2, \hat{l}_3)$ (a right-handed triad of perpendicular unit vectors) which is a principal axes system located at the center of mass. Let A denote the set of vectors

$$A = \{ \vec{a}^\alpha \mid \alpha = 1, 2, \dots, N \}, \quad (1)$$

where \vec{a}^α is the position vector from the origin of L to the point where the atom labelled by α is located. Each vector \vec{a}^α may be expressed relative to the frame L as

$$\vec{a}^\alpha = a_1^\alpha \hat{l}_1 + a_2^\alpha \hat{l}_2 + a_3^\alpha \hat{l}_3, \quad (2)$$

where $(a_1^\alpha, a_2^\alpha, a_3^\alpha)$ are specified real numbers.

Consider next the partitioning of A corresponding to sets of identical particles. Let A_k denote the subset of A consisting of position vectors of identical particles of "type k ". Then A may be written as the union of the disjoint subsets $\{A_k \mid k \in K\}$, where K is a set indexing the distinct types of atoms:

$$A = \bigcup_k A_k. \quad (3)$$

We now : the point group G of a molecule with static model A :

$$G = \{ R | R \in G \text{ and } R: A_k \rightarrow A_k, \text{ each } k \in K \}, \quad (4)$$

where G denotes the group of rotation-inversions of the space R^3 [Euclidean 3-space with points (x_1, x_2, x_3) which we will describe using the frame L].

We shall use the notation g to denote an element of the point group G .

There are two representations of the group G which play a significant rôle in this presentation:

(i) The representation of a proper rotation g as a linear transformation of the points of R^3 . In vector notation, we have

$$\begin{aligned} g: R^3 &\rightarrow R^3 \\ \vec{x} + \vec{y} = g \vec{x} &= \vec{x} \cos \phi + (\hat{n} \cdot \vec{x}) \hat{n} (1 - \cos \phi) \\ &+ (\hat{n} \times \vec{x}) \sin \phi, \end{aligned} \quad (5)$$

where g is a positive rotation (right-hand screw rule) by angle ϕ about the direction specified by the unit vector \hat{n} as determined from $g = R \in G$. g may also be represented by the 3×3 proper orthogonal matrix with element in row i and column j given by

$$R_{ij}(g) = \hat{l}_i \cdot g \hat{l}_j. \quad (6)$$

The inversion I of the space R^3 is defined by $I \vec{x} = -\vec{x}$ and is represented by $-I_3$, where I_3 denotes the 3×3 unit matrix.

(ii) The representation of g as a linear transformation on the elements of the set A . We may write

$$\begin{aligned} g: A &\rightarrow A \\ [\vec{a}^1 \vec{a}^2 \dots \vec{a}^N] &\rightarrow [\vec{a}^1 \vec{a}^2 \dots \vec{a}^N] P(g), \end{aligned} \quad (7)$$

where we have ordered the elements of A and placed them in a $1 \times N$ row vector. $P(g)$ is then an $N \times N$ permutation matrix.

Observe that the group multiplication properties are satisfied:

$$g'(g\vec{x}) = (g'g)\vec{x}, \text{ each } \vec{x} \in R^3,$$

$$\begin{aligned} R(g')R(g) &= R(g'g) , \\ P(g')P(g) &= P(g'g) , \end{aligned} \tag{8}$$

for all $g, g' \in G$. Thus, the two correspondences

$$g \rightarrow R(g) \text{ and } g \rightarrow P(g), \text{ each } g \in G, \tag{9}$$

are representations of the point group G .

If we denote by A the $3 \times N$ matrix

$$A = \begin{bmatrix} a_1^1 & a_1^2 & \dots & a_1^N \\ a_2^1 & a_2^2 & \dots & a_2^N \\ a_3^1 & a_3^2 & \dots & a_3^N \end{bmatrix}, \tag{10}$$

then A intertwines the representations $\{P(g) | g \in G\}$, that is,

$$R(g) A = A P(g), \text{ each } g \in G. \tag{11}$$

Relation (11) is the key result obtained from the static model of a rigid molecule.

Consider next the model for the motion of the molecule in space-time. Intuitively, we have in mind the following situation. We imagine that the rigid framework translates and rotates in space and that the atoms execute small oscillatory motions in the neighborhood of the (moving) equilibrium points. This intuitive picture for a set of motions of N particles corresponds to our conception of the motions (based on empirical knowledge) of what is today called a "rigid" molecule. There are sufficiently many molecules of the "rigid type" to justify a careful development of such a model. [A phenomenological model of a molecule such as this one clearly ignores many aspects of a "real molecule," and one does not expect the model to have general validity — the model is designed specifically for the description of vibration-rotation motions of the atoms, and even then for a limited energy domain.]

Even after settling on the model above, there are still many approaches that one might use to formulate a description of the motions. Let us continue the intuitive discussion. The use of a moving reference frame is suggested if one wishes to obtain a Hamiltonian for the system which, for motions in the neighborhood of the equilibrium configuration,

has the approximate form

$$T_{\text{C.M.}} + H_R + H_V, \quad (12)$$

where $T_{\text{C.M.}}$ is the kinetic energy of the center of mass, H_R the rotational energy, and H_V a Hamiltonian term for the kinetic and potential energies of the small motions near equilibrium. Intuition suggests the following forms for H_R and H_V :

$$H_R = \frac{J_1^2}{2I_1} + \frac{J_2^2}{2I_2} + \frac{J_3^2}{2I_3}, \quad (13)$$

$$H_V = \sum_{\mu=1}^{3N-6} (p_\mu^2 + \omega_\mu^2 q_\mu^2) / 2.$$

In the definition of H_R , the symbol J_i ($i=1,2,3$) denotes the component of the total angular momentum \vec{J} along the i -th axis of the moving frame; I_i is the principal moment of inertia of the equilibrium configuration about the i -th axis of the moving frame. (We choose the moving frame to coincide with a principal axis system when the atoms are located at their equilibrium points.) In the definition of H_V , the symbol q_μ ($\mu=1,2,\dots, 3N-6$) denotes a normal coordinate, p_μ its conjugate linear momentum, and ω_μ the frequency of the μ -th normal mode of oscillation. (The normal mode analysis of the vibrational motion may be carried out on the non-rotating molecule by several available methods.)

Let us next consider how one may give a precise formulation of the approach outlined above.

The first problem which must be solved is that of finding an appropriate moving reference frame. Eckart (5) solved this problem by imposing two conditions on the moving frame:

- (i) *Casimir's condition.* In the limit of vanishing displacements away from the equilibrium configuration, the Coriolis interaction between rotation and internal motions should be zero.
- (ii) *Linearity of internal coordinates.* The internal degrees of freedom should be described by coordinates which are linear combinations (with fixed numerical coefficients) of the components of the displacement away from equilibrium where the components are referred to the moving frame.

The second condition is imposed to assure that the normal coordinates calculated for the non-rotating molecule can be carried over, without change, to the rotating, vibrating molecule.

[We have gone to the trouble of briefly discussing the elementary (and standard) results above because the *Eckart frame* is

the key concept for understanding the rôle of the point group G in the molecular motions problem for rigid molecules.]

The explicit construction of the Eckart frame may be given in the following manner: (i) Introduce the three vectors \vec{F}_i defined by

$$\vec{F}_j = \sum_{\alpha} m_{\alpha} a_{\alpha j}^{\alpha} \vec{x}^{\alpha}, \quad (14)$$

where \vec{x}^{α} is the instantaneous position vector of atom α in the laboratory frame L . (ii) Define a triad of unit perpendicular vectors $(\hat{f}_1, \hat{f}_2, \hat{f}_3)$ by

$$\hat{f}_i = \sum_j (F^{-1/2})_{ij} \vec{F}_j, \quad (15)$$

where F denotes the symmetric Gram matrix with elements $F_{ij} = \vec{F}_i \cdot \vec{F}_j$. [We assume that $\vec{F}_1, \vec{F}_2, \vec{F}_3$ are linearly independent so that F is positive definite; $F^{-1/2}$ is then, by definition, the positive definite matrix such that $F^{-1/2} F^{-1/2} = F^{-1}$.] The three vectors $(\hat{f}_1, \hat{f}_2, \hat{f}_3)$ then define a moving frame F such that conditions (i) and (ii) above are satisfied.

Observe that the Eckart vectors depend implicitly on the particle position vectors \vec{x}^{α} . If we denote this result by writing $\hat{f}_i(\vec{x}^1, \dots, \vec{x}^N)$, then one easily verifies from Eqs. (14) and (15) that

$$\hat{f}_i(R\vec{x}^1, \dots, R\vec{x}^N) = (R\hat{f}_i)(\vec{x}^1, \dots, \vec{x}^N), \text{ each } R \in G, \quad (16)$$

$$\hat{f}_i(\vec{x}^1 + \vec{a}, \dots, \vec{x}^N + \vec{a}) = \hat{f}_i(\vec{x}^1, \dots, \vec{x}^N) \text{ for arbitrary translations } \vec{a}. \quad (17)$$

Thus, under an arbitrary rotation-inversion R of the molecule, the Eckart frame undergoes the same rotation-inversion. Under an arbitrary translation of the molecule, the Eckart frame is invariant. (It is this second property which allows us to consider that the Eckart frame is located at the center of mass of the moving molecule.)

Now that the moving reference frame F is defined (we consider only nonplanar molecules here), we may determine the transformation from the Cartesian coordinates $\lambda_i^{\alpha} = \vec{x}^{\alpha} \cdot \hat{e}_i$ relative to the laboratory frame to "molecular coordinates." The position vector of atom α is given by

$$\vec{x}^{\alpha} = \vec{R} + \vec{c}^{\alpha} + \vec{\rho}^{\alpha}, \quad (18)$$

where

- (i) \vec{R} is the instantaneous center of mass vector;
- (ii) \vec{c}^{α} is the position vector of the moving equilibrium point of atom α relative to the center of mass and of the form

$$\vec{c}^\alpha = a_1^\alpha \hat{f}_1 + a_2^\alpha \hat{f}_2 + a_3^\alpha \hat{f}_3 \quad (19)$$

when referred to the moving Eckart frame;

(iii) $\vec{\rho}^\alpha$ is the displacement vector of atom α from the equilibrium point $\vec{R} + \vec{c}^\alpha$.

There are six conditions imposed on the displacement vectors $\{\vec{\rho}^\alpha\}$:

$$\text{Center of mass condition: } \sum_{\alpha} m_{\alpha} \vec{\rho}^\alpha = \vec{0}, \quad (20)$$

$$\text{Eckart conditions: } \sum_{\alpha} m_{\alpha} \vec{c}^\alpha \times \vec{\rho}^\alpha = \vec{0}. \quad (21)$$

[The second set of conditions results from an easily proved relation between the Eckart frame vectors \hat{f}_i and the \vec{F}_i :

$$\hat{f}_1 \times \vec{F}_1 + \hat{f}_2 \times \vec{F}_2 + \hat{f}_3 \times \vec{F}_3 = \vec{0} .]$$

Let us call a set of vectors $\{\vec{\rho}^\alpha | \alpha = 1, \dots, N\}$ which satisfies Eqs. (20) and (21) a set displacement vectors for the frame $(\hat{f}_1, \hat{f}_2, \hat{f}_3)$.

It is convenient to reformulate Eqs. (20) and (21) in the form:

$$\sum_{\alpha} \vec{s}_i^\alpha \cdot \vec{\rho}^\alpha = 0, \quad (i = 1, 2, 3), \quad (20')$$

$$\sum_{\alpha} \vec{s}_i^\alpha \cdot \vec{\rho}^\alpha = 0, \quad (i = 4, 5, 6), \quad (21')$$

where

$$\begin{aligned} \vec{s}_i^\alpha &= m_{\alpha} \hat{f}_i / m^{1/2}, \quad m = \sum_{\alpha} m_{\alpha}, \\ \vec{s}_{i+3}^\alpha &= m_{\alpha} N_i^{-1/2} (\hat{f}_i \times \vec{c}^\alpha) \\ N_i &= \sum_{\alpha} m_{\alpha} (\hat{f}_i \times \vec{c}^\alpha) \cdot (\hat{f}_i \times \vec{c}^\alpha) \end{aligned} \quad (22)$$

for $i = 1, 2, 3$. Observe that the vectors in the set $\{\vec{s}_t^\alpha | t = 1, \dots, 6\}$ satisfy the orthogonality relations:

$$\sum_{\alpha} m_{\alpha}^{-1} \vec{s}_r^\alpha \cdot \vec{s}_t^\alpha = \delta_{rt}. \quad (23)$$

It is always possible (in infinitely many ways) to find additional vectors $\vec{s}_{\mu+6}^\alpha$, $\mu = 1, 2, \dots, 3N-6$, such that the $3N$ vectors in the set

$$\{\vec{s}_t^\alpha | t = 1, \dots, 3N\} \quad (24)$$

satisfy the orthogonality relations

$$\sum_{\alpha} m_{\alpha}^{-1} \vec{s}_r^\alpha \cdot \vec{s}_t^\alpha = \delta_{rt}. \quad (25)$$

Furthermore, all vectors \vec{s}_t^α may be chosen to have numerical components relative to the Eckart frame, that is,

$$s_{t,i}^{\alpha} \equiv \hat{s}_{t,i}^{\alpha} \cdot \hat{f}_i = \text{real numerical constant} . \quad (26)$$

These results all follow from the fact that it is possible to construct a $3N \times 3N$ orthogonal matrix with numerical entries in infinitely many ways when only the first six rows are specified (numerical) row vectors ($N \geq 3$).

The principal result obtained from the above analysis is: *The rotation-inversion invariants defined by*

$$Q_{\mu} = \sum_{\alpha} \hat{s}_{\mu+6}^{\alpha} \cdot \hat{\rho}^{\alpha} , \quad \mu = 1, 2, \dots, 3N-6 \quad (27)$$

span the $3N-6$ dimensional space of the internal coordinates.

[We use the term "span" here in the sense that each internal coordinate of the form $\xi = \sum_{\alpha} \xi^{\alpha} \cdot \hat{\rho}^{\alpha}$, ξ^{α} a triple of real numbers, has the form $\xi = \sum_{\mu} \xi_{\mu} Q_{\mu}$. Furthermore, $\sum_{\mu} a_{\mu} Q_{\mu} = \sum_{\mu} b_{\mu} Q_{\mu}$ implies $a_{\mu} = b_{\mu}$.]

Using Eqs. (20'), (21') and (25), we may invert Eq. (27) to obtain

$$\hat{\rho}^{\alpha} = m_{\alpha}^{-1} \sum_{\mu} \hat{s}_{\mu+6}^{\alpha} Q_{\mu} . \quad (28)$$

Taking components of Eq. (18) relative to the laboratory frame, we obtain the transformation:

$$\begin{aligned} x_i^{\alpha} &= R_i + \sum_j C_{ij} (a_j^{\alpha} + \rho_j^{\alpha}) , \\ \rho_j^{\alpha} &= m_{\alpha}^{-1} \sum_{\mu} s_{\mu+6,i}^{\alpha} Q_{\mu} . \end{aligned} \quad (29)$$

For each choice of the vectors $\hat{s}_{\mu+6}^{\alpha}$ ($\mu = 1, \dots, 3N-6$), Eqs. (29) define an explicit transformation from the $3N$ Cartesian coordinates $\{x_i^{\alpha}\}$ to the $3N$ coordinates

$$\begin{aligned} R_i \quad (i = 1, 2, 3); \quad C \quad (\text{containing } 3 \text{ independent coordinates}); \\ Q = \{Q_{\mu} | \mu = 1, \dots, 3N-6\} . \end{aligned} \quad (30)$$

Furthermore, the transformation (29) is invertible for those values of the $\{x_i^{\alpha}\}$ for which the Eckart frame construction exists ($\det F \neq 0$).

This completes the construction of the *dynamical molecular model*. Using the transformation (29) the classical Hamiltonian

$$H = \frac{1}{2} \sum_{\alpha,i} m_{\alpha} (\dot{x}_i^{\alpha})^2 + V(x_i^{\alpha}) \quad (31)$$

and the quantum mechanical Hamiltonian

$$H_{\text{op}} = -\frac{1}{2} \sum_{\alpha} \left(\frac{\partial}{\partial x_i^{\alpha}} \right)^2 + V(x_i^{\alpha}) \quad (32)$$

may be transformed unambiguously to the $3N$ molecular coordinates (30)

(confer Ref. 4). Furthermore, when the potential energy is approximated by a quadratic form in the internal coordinates $\{Q_\mu\}$, one obtains from Eqs. (31) and (32) approximate Hamiltonians of the forms (13).

We are now in a position to state the rôle of the point group G in the dynamical molecular model. We first define the action of the group G on a generic set $Y = \{\vec{y}^\alpha | \alpha = 1, 2, \dots, N\}$ of instantaneous position vectors relative to the center of mass: $\vec{y}^\alpha \equiv \vec{x}^\alpha - \vec{R}$. Consider the set of linear operators

$$L(G) = \{L_g | g \in G\}, \quad (33)$$

where $L_g: Y \rightarrow Z$ is the linear mapping of a set Y of instantaneous position vectors (relative to the center of mass) onto a second set Z of instantaneous position vectors (relative to the center of mass) given by

$$L_g: \vec{y}^\alpha \rightarrow \vec{z}^\alpha = L_g \vec{y}^\alpha = \sum_\beta (g \vec{y}^\beta) P_{\alpha\beta}(g) \quad (34)$$

in which

- (i) $\{P(g) | g \in G\}$ is the $N \times N$ permutation matrix representation (7) of G ;
- (ii) $g \vec{y}^\beta$ is the linear transformation defined for an arbitrary vector \vec{y} by

$$g \vec{y} = \sum_{ij} R_{ij}(g) (\vec{y} \cdot \hat{f}_j) \hat{f}_i, \quad (35)$$

where $\{R(g) | g \in G\}$ is the 3×3 orthogonal matrix representation (6) of G , and the Eckart frame vectors

\hat{f}_i ($i = 1, 2, 3$) are those corresponding to position vectors $\vec{y}^1, \dots, \vec{y}^N$, that is, $\hat{f}_i = \hat{f}_i(\vec{y}^1, \dots, \vec{y}^N)$.

Observe that $g \vec{y}^\alpha \cdot g \vec{y}^\beta = \vec{y}^\alpha \cdot \vec{y}^\beta$ so that g is a rotation-inversion and that $g'(g \vec{y}) = (g'g) \vec{y}$.

An alternative expression for the transformation (34) in terms of the components $\vec{y}^\alpha \cdot \hat{f}_i$ and $(L_g \vec{y}^\alpha) \cdot \hat{f}_i$ relative to the Eckart frame vectors $\hat{f}_i = \hat{f}_i(\vec{y}^1, \dots, \vec{y}^N)$ is

$$(L_g \vec{y}^\alpha) \cdot \hat{f}_i = \sum_{\beta, j} [P(g) \otimes R(g)]_{\alpha i; \beta j} \vec{y}^\beta \cdot \hat{f}_j, \quad (36)$$

where $P(g) \otimes R(g)$ is the (matrix) direct product of $P(g)$ with $R(g)$ and $[P(g) \otimes R(g)]_{\alpha i; \beta j} = P_{\alpha\beta}(g) R_{ij}(g)$ denotes the element of $P(g) \otimes P(g)$ in row αi and column βj .

The operators $\{L_g | g \in G\}$ satisfy the following relations:

$$\begin{aligned} \text{(i)} \quad & L_g (L_g \vec{y}^\alpha) = L_g \vec{y}^\alpha \text{ for arbitrary } \vec{y}^\alpha; \\ \text{(ii)} \quad & L_g \vec{c}^\alpha = \vec{c}^\alpha, \alpha = 1, 2, \dots, N; \\ \text{(iii)} \quad & L_g \hat{f}_i = \hat{f}_i, i = 1, 2, 3, \end{aligned} \quad (37)$$

where

$$(L_g \hat{f}_i)(\vec{y}^1, \dots, \vec{y}^N) \equiv \hat{f}_i(L_g \vec{y}^1, \dots, L_g \vec{y}^N).$$

The proofs of these relations are straightforward and may be found in Ref. 3.

Equation (i) means that the correspondence $g \rightarrow L_g$ is a *linear representation* of G ; Eq. (ii) means that G is an *isotropy group* of the set of vectors $\{\vec{c}^\alpha | \alpha = 1, \dots, N\}$ which define the static model [Eq. (11) for the static model provides the proof of (ii)]; and Eq. (iii) means that the Eckart frame is *invariant* under the action L_g of G .

Equations (37) are the key relations for establishing the rôle of the point group in the dynamical molecular model.

A principal result is: The group of operators

$$L(G) = \{L_g | g \in G\} \quad (38)$$

may be used to split the space of internal coordinates into subspaces which transform irreducibly under $L(G)$.

Proof. Let $\{\vec{\rho}^\alpha\}$ denote any set of displacement vectors for the frame $(\hat{f}_1, \hat{f}_2, \hat{f}_3)$. Since $L_g \vec{y}^\alpha = \vec{c}^\alpha + L_g \vec{\rho}^\alpha$, it follows that the set of vectors

$$\{L_g \vec{\rho}^\alpha | \alpha = 1, 2, \dots, N\} \quad (39)$$

is also a set of displacement vectors for the frame $(\hat{f}_1, \hat{f}_2, \hat{f}_3)$.

Now choose any basis set $\{Q_\mu | \mu = 1, \dots, 3N-6\}$ for the internal coordinates [cf. Eqs. (24)-(28)]. Since

$$(L_g \vec{\rho}^\alpha) \cdot \hat{f}_i = \sum_{\beta j} [P(g) \otimes R(g)]_{\alpha i, \beta j} \rho_j^\beta, \quad (40)$$

we find

$$L_g Q_\mu = \sum_\alpha s_{\mu+6}^\alpha \cdot (L_g \vec{\rho}^\alpha) = \sum_\nu M_{\mu\nu}(g) Q_\nu, \quad (41)$$

where

$$M_{\mu\nu}(g) = \sum_{\alpha i \beta j} m_\beta^{-1} s_{\mu+6, i}^\alpha s_{\nu+6, j}^\beta [P(g) \otimes R(g)]_{\alpha i, \beta j}. \quad (42)$$

The properties (i) $L_g L_g = L_{g'g}$ (group property) and (ii) $\sum_{\mu} a_{\mu} Q_{\mu} = \sum_{\mu} b_{\mu} Q_{\mu}$ implies $a_{\mu} = b_{\mu}$ (basis property) together imply that the set of matrices (dimension $3N-6$)

$$\{M(g) | g \in G\} \quad (43)$$

is a representation of G . The complete reduction of this representation into irreducible representations of G then defines internal coordinates of the form

$$\xi_{\gamma}^{\Gamma} = \sum_{\mu} a_{\gamma\mu}^{\Gamma} Q_{\mu}, \quad \gamma = 1, 2, \dots, \dim \Gamma, \quad (44)$$

which are transformed according to irreducible representation Γ of G under the action L_g of G .

We see from the above that the group of operators $L(G)$ solves fully the problem of classifying the internal coordinates according to their transformation properties under the irreducible representations of the point group G .

Let us next consider the rôle of the permutation group in the molecular model. The Schrödinger equation for a molecule (point atoms + point electrons + Coulomb interactions) is invariant under any permutation of the coordinates of identical particles. The model of a molecule which we have described will, in general, not be invariant under all permutations of identical atoms; this is because the general permutational symmetry may be broken by the choice of a *phenomenological potential energy function* which, in principle, allows one to distinguish spatially, in a finite time, between atoms that would otherwise be called identical. Said somewhat differently, the form of the phenomenological potential energy function might not admit tunneling effects, hence, no tunneling will be predicted by such a model. Before any molecular model is complete, one must choose (by specifying the potential energy function) which permutations of coordinates of identical atoms are to be allowed and which are not. (A bad choice may give a model whose predictions do not agree well with experiment.)

In the model of a "rigid" molecule, one implicitly assumes that no tunneling takes place. (This assumption is made when one chooses a potential energy function which keeps the atoms near their equilibrium positions.) The question then arises as to which permutations of coordinates of identical atoms are allowed by this model. The answer is easily given. Since the kinetic energy is invariant under the group P of all permutations of coordinates of identical atoms, it is the properties of the potential energy function alone under permutations of coordinates of identical atoms which restricts the symmetry of the

Hamiltonian to a subgroup of P . But, by assumption, the potential energy function V of a rigid molecule is the most general function of the internal coordinates $\{Q_u = 1, \dots, 3N-6\}$ which is analytic in the neighborhood of the equilibrium configuration and such that:

(i) Equilibrium conditions

$$\left. \frac{\partial V}{\partial Q_u} \right|_{\text{equilibrium}} = 0; \quad (45)$$

(ii) Invariance conditions

$$V(L_g Q_1, \dots, L_g Q_{3N-6}) = V(Q_1, \dots, Q_{3N-6}), \quad (46)$$

each $g \in G$. Thus, our problem is to determine the properties of the function (46) under permutations of coordinates of identical atoms.

In order to examine the above problem, we require a careful definition of "permutations of coordinates of identical particles" and the resulting properties of the internal coordinates under such permutations.

Let there be n_k identical atoms of type k labelled by distinct integers

$$\alpha_1(k), \alpha_2(k), \dots, \alpha_{n_k}(k),$$

and let the position vectors of these atoms in the laboratory frame be the vectors in the set X_k given by

$$X_k = \{\vec{x}^\alpha | \alpha = \alpha_1(k), \dots, \alpha_{n_k}(k)\}, \quad (47)$$

where \vec{x}^α is the position vector of the atom labelled α . A permutation P_k of the set of position vectors of the identical atoms of type k is a mapping of X_k onto X_k . The product of two permutations P'_k and P_k is then the usual composition of mappings. The set of all such mappings then forms a group isomorphic to the symmetric group S_{n_k} . Indexing the "types" of identical atoms by $k = 1, 2, \dots, m$ ($\sum_{k=1}^m n_k = N$), we see that $P_k P_{k'} = P_{k'} P_k$ ($k' \neq k$) on the set $X = \cup X_k$ and that each permutation $P: X \rightarrow X$ of position vectors of identical atoms of the molecule has the form

$$P = \prod_{k=1}^m P_k, \quad P_k \in S_{n_k}. \quad (48)$$

Consider next the linear mapping L_g defined by Eq. (34). Then the linear mapping $P_g: Y \rightarrow Y$ defined by

$$P_g = g L_g^{-1}, \quad \text{each } g \in G \quad (49)$$

is a permutation of position vectors (relative to the center of mass) of identical atoms:

$$P_g: \vec{y}^\alpha + P_g \vec{y}^\alpha = \sum_{\beta} \vec{y}^\beta P_{\beta\alpha}(g) . \quad (50)$$

Furthermore, the set of permutations which map Y onto Y given by

$$P(G) = \{P_g | g \in G\} \quad (51)$$

forms a group under composition of mappings; hence,

$$P_{g'}(P_g \vec{y}^\alpha) = P_{g'g} \vec{y}^\alpha . \quad (52)$$

The action of the group of permutations $P(G)$ on the vectors $\{\vec{c}^\alpha | \alpha = 1, \dots, N\}$ which give the equilibrium positions relative to the Eckart frame and the set of displacement vectors $\{\vec{\rho}^\alpha | \alpha = 1, \dots, N\}$ is given respectively by

$$P_g \vec{c}^\alpha = g \vec{c}^\alpha = \sum_{\beta} \vec{c}^\beta P_{\beta\alpha}(g) , \quad (53)$$

$$P_g \vec{\rho}^\alpha = g L_{g^{-1}} \vec{\rho}^\alpha = \sum_{\beta} \vec{\rho}^\beta P_{\beta\alpha}(g) . \quad (54)$$

Observe then that Eq. (52) is also valid when \vec{y}^α is replaced by \vec{c}^α or $\vec{\rho}^\alpha$.

The following useful properties of the permutations (50) may also be derived using the definition (49) or (50):

$$(i) \quad \hat{f}_1 (P_g \vec{y}^1, \dots, P_g \vec{y}^N) = (g \hat{f}_1) (\vec{y}^1, \dots, \vec{y}^N) . \quad (55)$$

This result states that the Eckart frame corresponding to the permuted position vectors $P_g \vec{y}^1, \dots, P_g \vec{y}^N$ is the rotation g of the frame F corresponding to the position vectors $\vec{y}^1, \dots, \vec{y}^N$.

$$(ii) \quad P_g Q_\mu = L_{g^{-1}} Q_\mu . \quad (56)$$

In this relation, $P_g Q_\mu$ is defined to be the result obtained from Q_μ by applying the permutation (50). Thus,

$$\begin{aligned} P_g Q_\mu &= \sum_{\alpha i} s_{\mu+6, i}^\alpha (g \hat{f}_1) \cdot (P_g \vec{\rho}^\alpha) \\ &= \sum_{\alpha i} s_{\mu+6, i}^\alpha \hat{f}_1 \cdot (g^{-1} P_g \vec{\rho}^\alpha) = \sum_{\alpha} \hat{s}_{\mu+6}^\alpha \cdot L_{g^{-1}} \vec{\rho}^\alpha \\ &= L_{g^{-1}} Q_\mu . \end{aligned} \quad (57)$$

$$(iii) \quad P_{g'} (P_g Q_\mu) = P_{g'g} Q_\mu = (g'^{-1} L_{g'^{-1}g}) (L_{g^{-1}} Q_\mu) . \quad (58)$$

This relation may be proved by applying $P_{g'}$ to the first line of Eq. (57). Thus,

$$\begin{aligned} P_{g'}(P_g Q_\mu) &= \sum_{\alpha i} s_{\mu+6,i}^\alpha [g'(\hat{g}f_i)] \cdot [P_{g'}(P_g \hat{\rho}^\alpha)] = P_{g'} P_g Q_\mu \\ &= \sum_{\alpha} \hat{s}_{\mu+6}^\alpha \cdot g^{-1} g'^{-1} P_{g'}(P_g \hat{\rho}^\alpha) = \sum_{\alpha} \hat{s}_{\mu+6}^\alpha \cdot (g^{-1} L_{g',-1} g) (L_{g,-1} \hat{\rho}^\alpha) \\ &= (g^{-1} L_{g',-1} g) (L_{g,-1} Q_\mu) . \end{aligned}$$

We can now state the first important result on the permutation symmetry of the potential energy function $V(Q_1, \dots, Q_{3N-6})$ of a rigid molecule: *The potential energy function $V(Q_1, \dots, Q_{3N-6})$ is invariant under the group $P(G)$:*

$$V(P_g Q_1, \dots, P_g Q_{3N-6}) = V(Q_1, \dots, Q_{3N-6}) , \quad (59)$$

each $g \in G$.

Proof. Confer Eqs. (57) and (46).

The second important result relates to the representation of the group $P(G)$ as a semi-direct product group: *The action of each permutation $P_g \in P(G)$ on the molecular coordinates $(F; Q)$, $F = (\hat{f}_1, \hat{f}_2, \hat{f}_3)$, $Q = (Q_1, \dots, Q_{3N-6})$ can be represented by the ordered pair, $P_g = (g, L_{g,-1})$,*

$$(g, L_{g,-1})(F; Q) = (gF; L_{g,-1}Q) , \quad (60)$$

where the multiplication rule for pairs is that of a semi-direct product:

$$(g', L_{g',-1})(g, L_{g,-1}) = (g'g, (g^{-1} L_{g',-1} g) L_{g,-1}) . \quad (61)$$

Proof. Confer Eqs. (55) and (58).

It is apparent from the preceding results that it is irrelevant as to which of the two groups $L(G)$ or $P(G)$ (each isomorphic to the point group G) we use to classify the internal coordinates according to their transformation properties under the irreducible representations of the point group G . In either case, it is the point group G itself which plays the fundamental rôle, and it is obtained from the static model of the molecule.

We have not yet encountered the feasible group. Let us now give its definition and discuss below its relation to the groups G , $L(G)$, and $P(G)$.

The feasible group $F(G)$ of a rigid molecule is the union

$$F(G) = F_+(G) \cup F_-(G) , \quad (62)$$

where $F_+(g)$ is the subgroup of $P(G)$ defined by

$$F_+(G) = \{P_g | g \in G \text{ and } \det R(g) = +1\} \quad (63)$$

and $F_-(G)$ is the set of operators defined by

$$F_-(G) = \{IP_g | g \in G \text{ and } \det R(g) = -1\} \quad (64)$$

in which I is the inversion operator on the space R^3 .

The action of the group $F(G)$ on the internal coordinates is the same as that of the group $P(G)$, since each of the internal coordinates Q_μ is invariant under inversion. The action of the two groups on the Eckart frame is, however, different, since

$$\begin{aligned} \hat{f}_i(P_g \vec{y}^1, \dots, P_g \vec{y}^N) &= (g \hat{f}_i) (\vec{y}^1, \dots, \vec{y}^N) , \\ \hat{f}_i(IP_g \vec{y}^1, \dots, IP_g \vec{y}^N) &= - (g \hat{f}_i) (\vec{y}^1, \dots, \vec{y}^N) . \end{aligned} \quad (65)$$

Thus, the action of each element of the feasible group on the Eckart frame is always a pure rotation.

Summary. The isomorphic groups $L(G)$, $P(G)$, and $F(G)$ have the actions on the molecular coordinates $(F;Q)$ given by

	F	Q
$L(G)$	g	L_g
$P(G)$	g	$L_{g^{-1}}$
$F(G)$	g for $\det g = +1$	$L_{g^{-1}}$
	$-g$ for $\det g = -1$	g^{-1}

Critique. The Hamiltonian H of Eq. (31) [and (32)] is invariant under all pure rotations and inversion of R^3 , and there is no apparent reason, in the case of rigid molecules, for introducing the feasible group since it occurs already as a subgroup of the group obtained by adjoining I to $P(G)$. This same criticism applies, of course, to non-rigid molecules: The Hamiltonian for a model of a non-rigid molecule will be invariant under all rotation-inversions of the space R^3 as well as some subgroup of the group of permutations of the position vectors of identical particles [cf. Eq. (48)], the particular subgroup being fixed by the properties of the potential energy function which is chosen for the model, this choice itself being based on physical considerations. It is therefore difficult to see the advantages of introducing the feasible group in place of conventional approaches.

I conclude with some remarks about the point group. Does the concept of a "point group" generalize to non-rigid molecules? Preliminary investigations (Ref. 6) indicate that it does for a class of such molecules, the key concepts being: (i) a definition of an appropriate body-fixed frame (or frames); and (ii) the definition of a group of transformations leaving the frame invariant.

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